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Magnetic and electrical studies of $Ho_{0.9}RE_{0.1}CrO_3$ (RE = Gd and Yb) multiferroics☆

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Summary We report magnetic and electrical studies on multiferroic systems $Ho_{0.9}(RE)_{0.1}CrO_3$ where RE symbolizes rare earths like Gd and Yb. Solid state diffusion method has been used to synthesize the samples. Structural phase formation has been confirmed with the help of powder X-ray diffraction. Magnetization measurements show canted antiferromagnetic nature with a weak ferromagnetic phase. Néel temperature for Cr^{3+}—Cr^{3+} ordering shifts to higher side with increasing radii of rare earth cations. Frequency (100 Hz to 1 MHz) and temperature (300—650 K) dependent resistivity measurements are suggestive of semiconducting nature of the samples.

Introduction

Perovskite oxides exhibit wide range of properties like magnetism, ferroelectricity, colossal magnetoresistance and metal to insulator transitions which makes them useful for technical applications (Benedek and Fennie, 2013; Béa et al., 2008; Rokhinson et al., 2012; Pantel et al., 2012). In recent past perovskites with a general formula $REMO_3$ (Moure and Peña, 2013) (where RE = rare earth ions and M = transition metal ions like Fe, Cr, Mn, etc.) have drawn considerable attention. Sahu et al. (2007) have reported multiferroic behaviour shown by heavy rare earth chromites $RECrO_3$. The studies elaborate that rare earth chromites exhibit canted antiferromagnetism and a ferroelectric transition (Sahu et al., 2007). Here we present results on the study of magnetic behaviour and electrical resistivity of substituted analogues of $HoCrO_3$ with 10 at.% substitutions of Gd and Yb for Ho.

Experimental details

Ceramic method has been used for the synthesis of the polycrystalline samples. Thoroughly grinded stoichiometric mixture of the oxides Ho_2O_3, Gd_2O_3, Yb_2O_3 and Cr_2O_3

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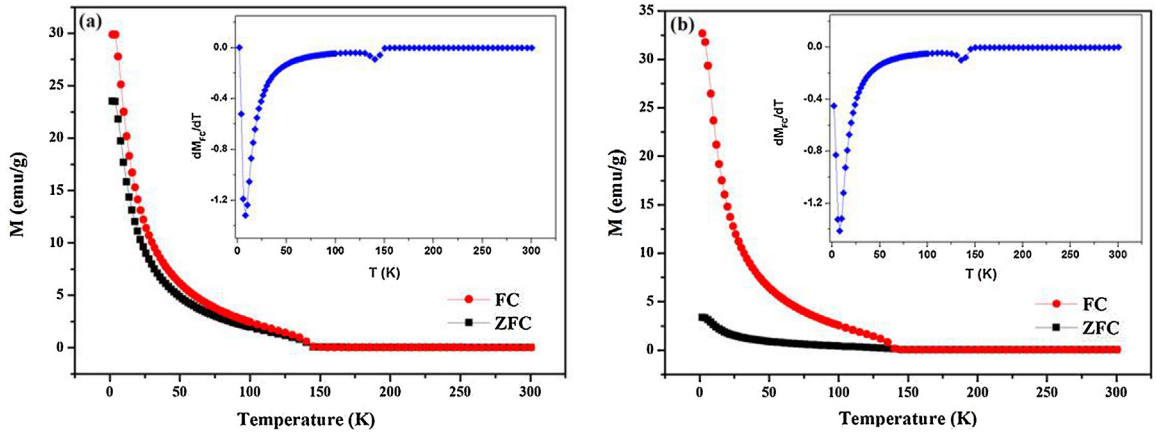

Figure 1 *M* vs *T* plot for the samples (a) HGCO and (b) HYCO.

(of a minimum of 3 N purity) was presintered at 900 °C for 24 h followed by one heating at 1300 °C for 24 h and a final heat treatment at 1400 °C for 24 h with grinding at intermediate stages. X-ray diffraction patterns confirmed formation of distorted orthorhombic phase. Prepared samples of $Ho_{0.9}Gd_{0.1}CrO_3$ and $Ho_{0.9}Yb_{0.1}CrO_3$ are referred to as HGCO and HYCO respectively.

DC magnetization measurements were performed using Quantum Design MPMS SQUID magnetometer. Magnetization vs temperature (*M*—*T*) data were recorded in the temperature range 2—300 K in both zero field cooled (ZFC) and field cooled (FC) modes under a magnetic field of 100 Oe. Magnetization—field (*M*—*H*) curves were recorded at 300 K and 5 K. Electrical resistivity measurements were made as a function of frequency (100 Hz to 1 MHz) and temperature (300—650 K) using a Wayne Kerr 6500B precision impedance analyzer.

Results and discussion

Magnetization measurements

Fig. 1 shows magnetization vs temperature (*M*—*T*) curves, for the two samples, in ZFC and FC modes. Coming from the high temperature side, ZFC and FC curves first show a kink — at 140 K for HGCO and 135 K for HYCO — and then depart from each other. Both FC and ZFC curves show continuously increasing magnetization down to the lowest measuring temperature, the departure being more pronounced in HYCO than in HGCO. Insets to figures show derivative d*M*(FC)/d*T* vs *T* of the FC data. Insets exhibit clear peaks at 140 K and 135 K for HGCO and HYCO respectively. In addition, the insets for both the samples show a peak at 7.6 K. In accordance with the reported studies on $HoCrO_3$ and other orthochromites (Sharma et al., 2010; Yuling et al., 2011), we assign the higher temperature anomaly T_{N1} to a paramagnetic to a canted antiferromagnetic (CAFM) alignment (weak ferromagnetic) of Cr^{3+} spins and the lower temperature anomaly T_{N2} to antiferromagnetic reorientation of RE spins. Slight reduction of T_{N1} is suggestive of reduction of the strength of Cr^{3+}—Cr^{3+} AFM interaction.

One stark contrast with the reported (Sharma et al., 2010; Yuling et al., 2011) magnetization studies on $HoCrO_3$ is that unlike in the case of the parent compound, the ZFC and FC curves of the two substituted analogues do not show magnetization reversal and no negative magnetization shows up. As regards FC curves, they have similar appearance to that reported for the parent compound. It is a surprising result that while both $HoCrO_3$ and $GdCrO_3$ show negative magnetization, this feature is missing in the substituted system $Ho_{0.9}Gd_{0.1}CrO_3$.

Now, magnetic behaviour in orthochromites like $GdCrO_3$, $La_{0.1}Gd_{0.9}CrO_3$ and $HoCrO_3$ has been explained (Sharma et al., 2010; Yuling et al., 2011; Su et al., 2011) in terms of the interactions Cr^{3+}—Cr^{3+}, Cr^{3+}—RE^{3+} and RE^{3+}—RE^{3+}. Magnetization reversal occurs due to the superposition of moments of the canted ordered sub-lattice of Cr^{3+} and the paramagnetic RE^{3+} aligned under the combined external magnetic field and internal magnetic field due to Cr^{3+} moments. Negative magnetization shows up below certain temperature when the moment of the RE sub-lattice is more than of the Cr sub-lattice. It also implies that the internal magnetic field due to the moments of the Cr sub-lattice is more than the external magnetic field. Absence of reversal of magnetization and of negative magnetization in the case of the samples under study imply that substitution of Gd and also of Yb have resulted in reduction of the moments of the Ho sub-lattice and also the internal magnetic field of the moments of Cr sub-lattice such that unlike in $HoCrO_3$ (i) the moment of the Ho sub-lattice is not more than of the Cr sub-lattice and (ii) internal magnetic field due to the moments of the Cr sub-lattice is not more than the external magnetic field.

Inverse susceptibility shows a linear variation with temperature in the paramagnetic region showing that the two samples follow Curie—Weiss law which is suggestive of localized magnetic behaviour. Obtained paramagnetic Néel temperature for both the samples is −24.7 K. Reported value (Su et al., 2011) for the unsubstituted parent compound is −24 K.

Fig. 2 shows magnetization—field (*M*—*H*) curves, at 5 K and 300 K, for the two samples. At 300 K the samples are paramagnetic and at 5 K, both the samples exhibit hysteresis. Coercivity for HGCO and HYCO at 5 K are ∼0.45 T and 0.25 T to be compared with (Yuling et al., 2011) ∼1.2 T for $HoCrO_3$ at 10 K. Further, unlike in the case of $HoCrO_3$ wherein *M* does not show saturating trend (upto 4 T field), for the two substituted samples, *M* shows near saturation.

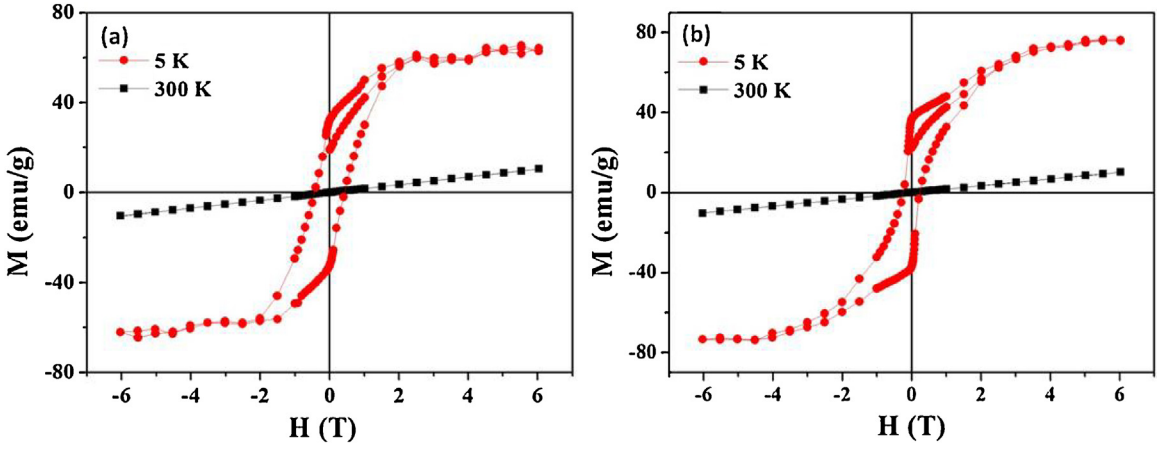

Figure 2 *M*—*H* hysteresis loop for (a) HGCO and (b) HYCO.

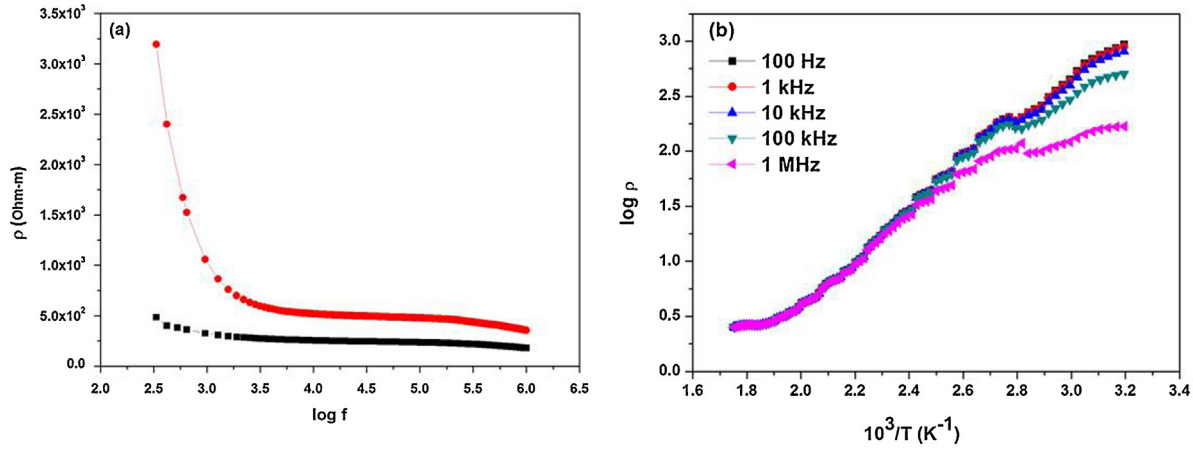

Figure 3 (a) ρ vs log f for HGCO (—■—) and HYCO (—●—) at 300 K and (b) log ρ vs $10^3/T$ for HGCO at different frequencies.

The saturation moment for HYCO is more than for HGCO. The reported value (Su et al., 2011) for $HoCrO_3$ at 10 K and 4 T field is ~80 emu/g. For the samples under study the values at 5 K and 4 T field are 60 emu/g and 70 emu/g for HGCO and HYCO respectively. This shows that the two substituted samples exhibit less anisotropy (more so with Yb substitution) but less magnetization vis-à-vis the parent compound.

Electrical resistivity measurements

Fig. 3(a) shows variation of electrical resistivity with frequency (ρ — log f) for the two samples at 300 K. ρ decreases with increasing f. Increase in frequency of the external field stimulates the hopping of charge carriers thereby resulting in enhanced conduction and lower resistivity (Watawe et al., 2000). In lower frequency regime Yb^{3+} substituted sample exhibits higher order of ρ than does the Gd^{3+} substituted sample. Fig. 3(b) shows, for HGCO, log ρ vs $10^3/T$ at different frequencies. For HYCO, log ρ shows similar T^{-1} dependence. The variation suggests semiconducting nature. Decrease in resistivity with increase in temperature owes to the increase in thermally activated drift mobility of charge carriers and is in accordance with the hopping conduction mechanism (Patil and Chogule, 2009). At higher temperatures the curves for different frequencies merge into one.

Conclusion

Magnetic and electrical resistivity studies have been conducted on multiferroic orthochromite system $Ho_{0.9}RE_{0.1}CrO_3$ (where RE = Gd and Yb). Magnetization measurements show two magnetic transitions, viz., paramagnetic to a canted antiferromagnetic (CAFM) phase of Cr sublattice — weak ferromagnetic (FM) and canted CAFM phase of RE sublattice at 140 K and 7.6 K for HGCO and 135 K and 7.6 K for HYCO. Substitutions cause weakening of Cr^{3+}—Cr^{3+} interaction, weakening of magnetic anisotropy and reduction of the CAFM moment. The samples do not exhibit negative magnetization implying reduction of Ho moments and weakening of the internal field of Cr sublattice. Electrical resistivity measurements are suggestive of semiconducting nature of the samples.

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